

XIV. "On the Properties of Silicic Acid and other analogous Colloidal Substances." By THOMAS GRAHAM, F.R.S., Master of the Mint. Received June 16, 1864.

(Preliminary Notice.)

The prevalent notions respecting solubility have been derived chiefly from observations on crystalline salts, and are very imperfectly applicable to the class of colloidal substances. Hydrated silicic acid, for instance, when in the soluble condition, is properly speaking a liquid body, like alcohol, miscible with water in all proportions. We have no degrees of solubility to speak of with respect to silicic acid, like the degrees of solubility of a salt, unless it be with reference to silicic acid in the gelatinous condition, which is usually looked upon as destitute of solubility. The jelly of silicic acid may be more or less rich in combined water, as it is first prepared, and it appears to be soluble in proportion to the extent of its hydration. A jelly containing 1 per cent. of silicic acid, gives with cold water a solution containing about 1 of silicic acid in 5000 water; a jelly containing 5 per cent. of silicic acid, gives a solution containing about 1 part of acid in 10,000 water. A less hydrated jelly than the last mentioned is still less soluble; and finally, when the jelly is rendered anhydrous, it gives gummy-looking white masses, which appear to be absolutely insoluble, like the light dusty silicic acid obtained by drying a jelly charged with salts, in the ordinary analysis of a silicate.

The liquidity of silicic acid is only affected by a change, which is permanent (namely, coagulation or pectization), by which the acid is converted into the gelatinous or pectous form, and loses its miscibility with water. The liquidity is permanent in proportion to the degree of dilution of silicic acid, and appears to be favoured by a low temperature. It is opposed, on the contrary, by concentration, and by elevation of temperature. A liquid silicic acid of 10 or 12 per cent. pectizes spontaneously in a few hours at the ordinary temperature, and immediately when heated. A liquid of 5 per cent. may be preserved for five or six days; a liquid of 2 per cent. for two or three months; and a liquid of 1 per cent. has not pectized after two years. Dilute solutions of 0.1 per cent. or less are no doubt practically unalterable by time, and hence the possibility of soluble silicic acid existing in nature. I may add, however, that no solution, weak or strong, of silicic acid in water has shown any disposition to deposit *crystals*, but always appears on drying as a colloidal glassy hyalite. The formation of quartz crystals at a low temperature, of so frequent occurrence in nature, remains still a mystery. I can only imagine that such crystals are formed at an inconceivably slow rate, and from solutions of silicic acid which are extremely dilute. Dilution no doubt weakens the colloidal character of substances, and may therefore allow their crystallizing tendency to gain ground and develop itself, particularly where the crystal once formed is completely insoluble, as with quartz.

The pectization of liquid silicic acid is expedited by contact with solid matter in the form of powder. By contact with pounded graphite, which is chemically inactive, the pectization of a 5 per cent. silicic acid is brought about in an hour or two, and that of a 2 per cent. silicic acid in two days. A rise of temperature of  $1^{\circ}1$  C. was observed during the formation of the 5 per cent. jelly.

The ultimate pectization of silicic acid is preceded by a gradual thickening in the liquid itself. The flow of liquid colloids through a capillary tube is always slow compared with the flow of crystalloid solutions, so that a liquid-transpiration-tube may be employed as a colloidoscope. With a colloidal liquid alterable in viscosity, such as silicic acid, the increased resistance to passage through the colloidoscope is obvious from day to day. Just before gelatinizing, silicic acid flows like an oil.

A dominating quality of colloids is the tendency of their particles to adhere, aggregate, and contract. This idio-attraction is obvious in the gradual thickening of the liquid, and when it advances leads to pectization. In the jelly itself, the specific contraction in question, or *synæresis*, still proceeds, causing separation of water, with the division into a clot and serum; and ending in the production of a hard stony mass, of vitreous structure, which may be anhydrous, or nearly so, when the water is allowed to escape by evaporation. The intense *synæresis* of isinglass dried in a glass dish over sulphuric acid *in vacuo*, enables the contracting gelatin to tear up the surface of the glass. Glass itself is a colloid, and the adhesion of colloid to colloid appears to be more powerful than that of colloid to crystalloid. The gelatin, when dried in the manner described upon plates of calc-spar and mica, did not adhere to the crystalline surface, but detached itself on drying. Polished plates of glass must not be left in contact, as is well known, owing to the risk of permanent adhesion between their surfaces. The adhesion of broken masses of glacial phosphoric acid to each other is an old illustration of colloidal *synæresis*.

Bearing in mind that the colloidal phasis of matter is the result of a peculiar attraction and aggregation of molecules, properties never entirely absent from matter but greatly more developed in some substances than in others, it is not surprising that colloidal characters spread on both sides into the liquid and solid conditions. These characters appear in the viscosity of liquids, and in the softness and adhesiveness of certain crystalline substances. Metaphosphate of soda, after fusion by heat, is a true glass or colloid; but when this glass is maintained for a few minutes at a temperature some degrees under its point of fusion, the glass assumes a crystalline structure without losing its transparency. Notwithstanding this change, the low diffusibility of the salt is preserved, with other characters of a colloid. Water in the form of ice has already been represented as a similar intermediate form, both colloid and crystalline, and in the first character adhesive and capable of reunion or "regelation."

It is unnecessary to return here to the fact of the ready pectization of

liquid silicic acid by alkaline salts, including some of very sparing solubility, such as carbonate of lime, beyond stating that the presence of carbonate of lime in water was observed to be incompatible with the coexistence of soluble silicic acid, till the proportion of the latter was reduced to nearly 1 in 10,000 water.

Certain liquid substances differ from the salts in exercising little or no pectizing influence upon liquid silicic acid. But, on the other hand, none of the liquids now referred to appear to conduce to the preservation of the fluidity of the colloid, at least not more than the addition of water would do. Among these inactive diluents of silicic acid are found hydrochloric, nitric, acetic, and tartaric acids, syrup of sugar, glycerine, and alcohol. But all the liquid substances named, and many others, appear to possess an important relation to silicic acid, of a very different nature from the pectizing action of salts. They are capable of displacing the combined water of the silicic acid hydrate, whether that hydrate is in the liquid or gelatinous condition, and give new substitution-products.

A liquid compound of *alcohol* and silicic acid is obtained by adding alcohol to aqueous silicic acid, and then employing proper means to withdraw the water from the mixture. For that purpose the mixture contained in a cup may be placed over dry carbonate of potash or quicklime, within the receiver of an air-pump. Or a dialyzing bag of parchment-paper containing the mixed alcohol and silicic acid may be suspended in a jar of alcohol: the water diffuses away, leaving in the bag a liquid composed of alcohol and silicic acid only. A point to be attended to is, that the silicic acid should never be allowed to form more than 1 per cent. of the alcoholic solution, otherwise it may gelatinize during the experiment. If I may be allowed to distinguish the liquid and gelatinous hydrates of silicic acid by the irregularly formed terms of *hydrosol* and *hydrogel* of silicic acid, the two corresponding alcoholic bodies now introduced may be named the *alcosol* and *alcogel* of silicic acid.

The *alcosol* of silicic acid, containing 1 per cent. of the latter, is a colourless liquid, not precipitated by water or salts, nor by contact with insoluble powders, probably from the small proportion of silicic acid present in solution. It may be boiled and evaporated without change, but is gelatinized by a slight concentration. The alcohol is retained less strongly in the *alcosol* of silicic acid than water is in the *hydrosol*, but with the same varying force, a small portion of the alcohol being held so strongly as to char when the resulting jelly is rapidly distilled at a high temperature. Not a trace of silicic ether is found in any compound of this class. The jelly burns readily in the air, leaving the whole silicic acid in the form of a white ash.

The *alcogel*, or solid compound, is readily prepared by placing masses of gelatinous silicic acid, containing 8 or 10 per cent. of the dry acid, in absolute alcohol, and changing the latter repeatedly till the water of the *hydrogel* is fully replaced by alcohol. The *alcogel* is generally slightly opalescent,

and is similar in aspect to the hydrogel, preserving very nearly its original bulk. The following is the composition of an alcogel carefully prepared from a hydrogel which contained 9·35 per cent. of silicic acid :—

|                    |              |
|--------------------|--------------|
| Alcohol .....      | 88·13        |
| Water.....         | 0·23         |
| Silicic acid ..... | 11·64        |
|                    | <hr/> 100·00 |

Placed in water, the alcogel is gradually decomposed—alcohol diffusing out and water entering instead, so that a hydrogel is reproduced.

Further, the alcogel may be made the starting-point in the formation of a great variety of other substitution jellies of analogous constitution, the only condition required appearing to be that the new liquid and alcohol should be intermiscible, that is, interdiffusible bodies. Compounds of ether, benzole, and bisulphide of carbon have thus been produced. Again, from *etherogel* another series of silicic acid jellies may be derived, containing fluids soluble in ether, such as the fixed oils.

The preparation of the *glycerine* compound of silicic acid is facilitated by the comparative fixity of that liquid. When hydrated silicic acid is first steeped in glycerine, and then boiled in the same liquid, water distils over, without any change in the appearance of the jelly, except that when formerly opalescent it becomes now entirely colourless, and ceases to be visible when covered by the liquid. But a portion of the silicic acid is dissolved, and a *glycerosol* is produced at the same time as the glycerine jelly. A glycerogel prepared from a hydrate containing 9·35 per cent. of silicic acid, was found by a combustion analysis to be composed of

|                   |              |
|-------------------|--------------|
| Glycerine .....   | 87·44        |
| Water.....        | 3·78         |
| Silicic acid..... | 8·95         |
|                   | <hr/> 100·17 |

The glycerogel has somewhat less bulk than the original hydrogel. When a glycerine jelly is distilled by heat, it does not fuse, but the whole of the glycerine comes over, with a slight amount of decomposition towards the end of the process.

The compound of sulphuric acid, *sulphagel*, is also interesting from the facility of its formation, and the complete manner in which the water of the original hydrogel is removed. A mass of hydrated silicic acid may be preserved unbroken if it is first placed in sulphuric acid diluted with two or three volumes of water, and then transferred gradually to stronger acids, till at last it is placed in concentrated oil of vitriol. The sulphagel sinks in the latter fluid, and may be distilled with an excess of it for hours without losing its transparency or gelatinous character. It is always somewhat less in bulk than the primary hydrogel, but not more, to the eye, than one-fifth or one-sixth part of the original volume. This sulphagel is transparent and

colourless. When a sulphagel is heated strongly in an open vessel, the last portions of the monohydrated sulphuric acid in combination are found to require a higher temperature for their expulsion than the boiling-point of the acid. The whole silicic acid remains behind, forming a white, opaque, porous mass, like pumice. A sulphagel placed in water is soon decomposed, and the original hydrogel reproduced. No permanent compound of sulphuric and silicic acids, of the nature of a salt, appears to be formed in any circumstances. A sulphagel placed in alcohol gives ultimately a pure alcogel. Similar jellies of silicic acid may readily be formed with the monohydrates of nitric, acetic, and formic acids, and are all perfectly transparent.

The production of the compounds of silicic acid now described indicates the possession of a wider range of affinity by a colloid than could well be anticipated. The organic colloids are no doubt invested with similar wide powers of combination, which may become of interest to the physiologist. The capacity of a mass of gelatinous silicic acid to assume alcohol, or even oleine, in the place of water of combination, without disintegration or alteration of form, may perhaps afford a clue to the penetration of the albuminous matter of membrane by fatty and other insoluble bodies, which seems to occur in the digestion of food. Still more remarkable and suggestive are the *fluid* compounds of silicic acid. The fluid alcohol-compound favours the possibility of the existence of a compound of the colloid albumen with oleine, soluble also and capable of circulating with the blood.

The feebleness of the force which holds together two substances belonging to different physical classes, one being a colloid and the other a crystalloid, is a subject deserving notice. When such a compound is placed in a fluid, the superior diffusive energy of the crystalloid may cause its separation from the colloid. Thus, of hydrated silicic acid, the combined water (a crystalloid) leaves the acid (a colloid) to diffuse into alcohol; and if the alcohol be repeatedly changed, the entire water is thus removed, alcohol (another crystalloid) at the same time taking the place of water in combination with the silicic acid. The liquid in excess (here the alcohol) gains entire possession of the silicic acid. The process is reversed if an alcogel be placed in a considerable volume of water. Then alcohol separates from combination, in consequence of the opportunity it possesses to diffuse into water; and water, which is now the liquid present in excess, recovers possession of the silicic acid. Such changes illustrate the predominating influence of mass.

Even the compounds of silicic acid with alkalis yield to the decomposing force of diffusion. The compound of silicic acid with 1 or 2 per cent. of soda is a colloidal solution, and, when placed in a dialyzer over water *in vacuo* to exclude carbonic acid, suffers gradual decomposition. The soda diffuses off slowly in the caustic state, and gives the usual brown oxide of silver when tested with the nitrate of that base.

The pectionization of liquid silicic acid and many other liquid colloids is effected by contact with minute quantities of salts in a way which is not

understood. On the other hand, the gelatinous acid may again be liquefied and have its energy restored by contact with a very moderate amount of alkali. The latter change is gradual, 1 part of caustic soda, dissolved in 10,000 water, liquefying 200 parts of silicic acid (estimated dry) in 60 minutes at 100° C. Gelatinous stannic acid also is easily liquefied by a small proportion of alkali, even at the ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again from it by diffusion into water upon a dialyzer. The solution of these colloids, in such circumstances, may be looked upon as analogous to the solution of insoluble organic colloids witnessed in animal digestion, with the difference that the solvent fluid here is not acid but alkaline. Liquid silicic acid may be represented as the "peptone" of gelatinous silicic acid; and the liquefaction of the latter by a trace of alkali may be spoken of as the peptization of the jelly. The pure jellies of alumina, peroxide of iron, and titanitic acid, prepared by dialysis, are assimilated more closely to albumen, being peptized by minute quantities of hydrochloric acid.

*Liquid Stannic and Metastannic Acids.*—Liquid stannic acid is prepared by dialyzing the bichloride of tin with an addition of alkali, or by dialyzing the stannate of soda with an addition of hydrochloric acid. In both cases a jelly is first formed on the dialyzer; but, as the salts diffuse away, the jelly is again peptized by the small proportion of free alkali remaining: the alkali itself may be removed by continued diffusion, a drop or two of the tincture of iodine facilitating the separation. The liquid stannic acid is converted on heating it into liquid metastannic acid. Both liquid acids are remarkable for the facility with which they are peptized by a minute addition of hydrochloric acid, as well as by salts.

*Liquid Titanic Acid* is prepared by dissolving gelatinous titanitic acid in a small quantity of hydrochloric acid, without heat, and placing the liquid upon a dialyzer for several days. The liquid must not contain more than 1 per cent. of titanitic acid, otherwise it spontaneously gelatinizes, but it appears more stable when dilute. Both titanitic and the two stannic acids afford the same classes of compounds with alcohol &c. as are obtained with silicic acid.

*Liquid Tungstic Acid.*—The obscurity which has so long hung over tungstic acid is removed by a dialytic examination. It is in fact a remarkable colloid, of which the pectous form alone has hitherto been known. Liquid tungstic acid is prepared by adding dilute hydrochloric acid carefully to a 5 per cent. solution of tungstate of soda, in sufficient proportion to neutralize the alkali, and then placing the resulting liquid on a dialyser. In about three days the acid is found pure, with the loss of about 20 per cent., the salts having diffused entirely away. It is remarkable that the *purified* acid is not peptized by acids or salts even at the boiling temperature. Evaporated to dryness, it forms vitreous scales, like gum or gelatin, which sometimes adhere so strongly to the surface of the evaporating dish as to detach portions of it. It may be heated to 200° C.

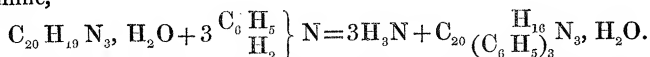
without losing its solubility or passing into the pectous state, but at a temperature near redness it undergoes a molecular change, losing at the same time 2·42 per cent. of water. When water is added to unchanged tungstic acid, it becomes pasty and adhesive like gum; and it forms a liquid with about one-fourth its weight of water, which is so dense as to float glass. The solution effervesces with carbonate of soda, and tungstic acid is evidently associated with silicic and molybdic acids. The taste of tungstic acid dissolved in water is not metallic or acid, but rather bitter and astringent. Solutions of tungstic acid containing 5, 20, 50, 66·5, and 79·8 per cent. of dry acid, possess the following densities at 19°, 1·0475, 1·2168, 1·8001, 2·396, and 3·243. Evaporated *in vacuo* liquid tungstic acid is colourless, but becomes green in air from the deoxidating action of organic matter. Liquid silicic acid is protected from pectizing when mixed with tungstic acid, a circumstance probably connected with the formation of the double compounds of these acids which M. Marignac has lately described.

*Molybdic Acid* has hitherto been known (like tungstic acid) only in the insoluble form. Crystallized molybdate of soda dissolved in water is decomposed by the gradual addition of hydrochloric acid in excess without any immediate precipitation. The acid liquid thrown upon a dialyzer may gelatinize after a few hours, but again liquefies spontaneously, when the salts diffuse away. After a diffusion of three days, about 60 per cent. of the molybdic acid remains behind in a pure condition. The solution of pure molybdic acid is yellow, astringent to the taste, acid to test-paper, and possesses much stability. The acid may be dried at 100°, and then heated to 200° without losing its solubility. Soluble molybdic acid has the same gummy aspect as soluble tungstic acid, and deliquesces slightly when exposed to damp air. Both acids lose their colloidal nature when digested with soda for a short time, and give a variety of crystallizable salts.

XV. "Researches on the Colouring-matters derived from Coal-tar. —III. Diphenylamine." By A. W. HOFMANN, LL.D., F.R.S., Received June 16, 1864.

In the course of last year\* I published an account of some experiments upon the composition of the blue colouring-matter discovered by MM. Girard and De Laire when studying the action of aniline upon rosaniline.

These experiments had established a simple relation between aniline-red and aniline-blue, the latter exhibiting the composition of triphenylated rosaniline,



The composition of aniline-blue has since been also investigated by M. Schiff†, who, in a paper published shortly after my first communication

\* Proceedings of the Royal Society, vol. xii. p. 578; and vol. xiii. p. 9.

† Comptes Rendus, lvi. 1234.